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IMPROVED SYSTHESIS OF BENZIL END-CAPPED ACETYLENE  
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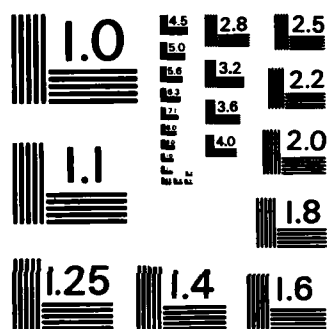
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IMPROVED SYNTHESIS OF BENZIL END-CAPPED  
ACETYLENE TERMINATED PHENYLQUINOXALINE  
RESINS

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Polymer Branch  
Nonmetallic Materials Division

May 1985

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Final Report for Period June 1980 - August 1982

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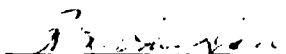
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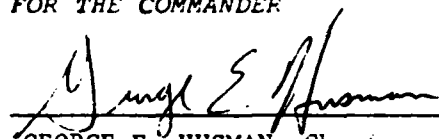


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# FOREWORD

This in-house report was prepared by the Polymer Branch, Nonmetallic Materials Division. This work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFWAL/ML Work Unit Scientist. This report describes work conducted June 1980 to August 1982.

The work described in this report was conducted by Dr. F. L. Hedberg, 1st Lt Patricia M. Lindley, and Marilyn E. Hunsaker. The manuscript was released by the authors in December 1982 for publication as a Technical Report.

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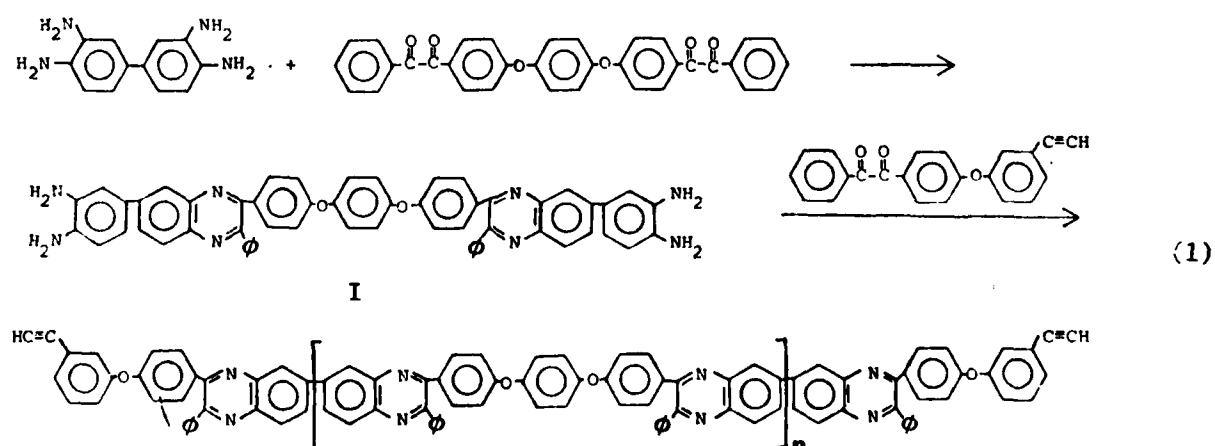
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# SECTION I

## INTRODUCTION

Recent work in our laboratory has focused on a family of benzil end-capped acetylene terminated phenylquinoxalines designated as "BATQ's" (Reference 1). These systems are of interest because they provide great potential for both high temperature resistance and high moisture insensitivity. The acetylene end groups allow thermal homopolymerization via nonvolatile addition reactions which occur at 200-250°C. These reactions generate a fused aromatic system with excellent thermo-oxidative stability. At the same time, the presence of the phenylquinoxaline backbone provides the high temperature stability generally associated with heterocycles.

The BATQ's are derived synthetically from the reaction of 3,3'-diaminobenzidine (DAB) with a bis-benzil in 2:1 stoichiometry followed by an end-capping reaction on the tetraamine intermediate by 4-(3-ethynylphenoxy)benzil. The BATQ system most studied in our laboratory is BATQ-H based upon 1,4-bis(4-benzilyloxy)benzene (Equation 1).





Because of unavoidable formation of a certain amount of tetraamine end-capped oligomer ( $n > 1$ ) in the first step of the synthesis, an equivalent molar amount of unreacted DAB remains and reacts with 4-(3-ethynylphenoxy)-benzil to form an  $n=0$  chain length component of BATQ-H which is a mixture of 2,2'-bis(4-[3-ethynylphenoxy]phenyl)-3,3'-diphenyl-6,6'-biquinoxaline together with the 3,3'-2,2' and 2,3'-2',3 isomers. This isomer mixture, collectively designated as BA-DAB-BA, has been synthesized previously (Reference 1). The ultimate composition of BATQ-H therefore consists predominantly of the stoichiometric  $n=1$  chain length product together with significant amounts of  $n=0$  and  $n > 1$  chain length products.

Separate studies have been recently undertaken in this laboratory on the potential of BA-DAB-BA for composite resin and adhesive applications (Reference 2), and on the potential of BATQ-H for composite resin applications (Reference 3). In connection with these studies, the original synthesis (Reference 1) of BA-DAB-BA and BATQ-H have been improved substantially with respect to both ease of procedure and purity of product. A method was also developed for selective removal of BA-DAB-BA from BATQ-H in order to satisfy a requirement for chain length control to correlate chain length with toughness.

## SECTION II

### RESULTS AND DISCUSSION

#### A. Preparation of BA-DAB-BA

In the original preparation of BA-DAB-BA, an overnight reaction between DAB and 4-(3-ethynylphenoxy)benzil was carried out in tetrahydrofuran catalyzed by acetic acid. This procedure required precipitation from a large volume of water followed by an extraction procedure due to the difficulties encountered in attempting to filter the fine suspension formed. A subsequent precipitation from a methylene chloride-ethyl acetate solution into methanol was required to achieve high purity. We have found that this procedure can be greatly simplified by the use of methanol containing a catalytic amount of acetic acid as the reaction solvent. The BA-DAB-BA precipitated from solution as it was formed, and had only to be collected and washed with methanol to afford a pure product. The smaller volumes of solvent required made this procedure very amenable to scale-up, and this is, therefore, the recommended preparative method for BA-DAB-BA.

#### B. Preparation of BATQ-H

The original procedure for the synthesis of BATQ-H in accordance with equation 1, was carried out at 90-100°C. We have found that these temperature conditions are not only unnecessary, but actually detrimental, and that the reaction sequence will go to completion in a relatively short period of time at ambient temperature. Ambient temperature conditions provide a number of advantages such as elimination of both equipmental and energy requirements associated with heating. The major improvement, however, is the substantially greater purity of product obtained at ambient conditions.

With the heated reaction a certain amount of  $R_f$  zero material is always seen when thin layer chromatography is used to analyze the product. This material may be caused by decomposition of either 3,3'-diaminobenzidine or the intermediate amine end-capped oligomer mixture ( $I, n \geq 1$ ). If either amine group of an o-diamine is destroyed, no end-capping reaction with 4-(3-ethynylphenoxy)benzene can occur. Indeed, infrared analysis indicates the presence of an amine or hydroxyl-type moiety in the product. This low  $R_f$  material is not present in the product obtained from the room temperature reaction.

Liquid chromatography of samples obtained under both conditions also support the ambient conditions as yielding a cleaner product. Peaks are very sharp and well-defined for the various oligomers formed at room temperature, while a more ragged spectrum with some shoulder peaks results when the heated sample is chromatographed.

A further difference between the two samples can be seen in changes in the reactivity of the materials. The product obtained at room temperature has a much higher reactivity than the material which was formed by heating (Reference 4). This may also be due to the presence of low  $R_f$  impurities which inhibit the polymerization in the sample prepared by the old method.

Aside from the effect on the reactivity of the impurities present, there are other factors which influence the polymerization reaction in both the heated and unheated samples. The presence of BA-DAB-BA and the  $n \geq 1$  oligomers exerts a great influence on the cure behavior and properties of the system.

Normally, BATQ samples have a  $T_g$  of 140-170°C. It has been found that the presence of BA-DAB-BA and of high oligomers exerts a great effect on the softening temperature, even at relatively low concentrations (12%). The oligomers also have the effect of lowering the final  $T_g$  of the polymer while improving mechanical properties, due to a large molecular weight between crosslinks.

The presence of BA-DAB-BA in the system exerts the major influence which lowers the softening temperature of a BATQ sample. BA-DAB-BA alone has a softening range of 75-100°C, and with the high Tg of the material after cure it appears to offer very desirable characteristics as a reactive diluent for BATQ. Unfortunately, there are also problems associated with the use of this  $n=0$  component, primarily because it has a low molecular weight between crosslinks that may lower the mechanical properties of the final resin.

The reactive diluent characteristics of BA-DAB-BA which aid in broadening the processing window led to a search for better diluents which would not have the negative effect on mechanical properties. Work with 1-phenoxy-3-(3-ethynylphenoxy)benzene has been very encouraging and has eliminated the need for BA-DAB-BA in BATQ samples (Reference 5).

When it became desirable to eliminate as much BA-DAB-BA as possible from the BATQ-H, work was initiated to develop a precipitation system which would preferentially remove the BA-DAB-BA  $n=0$  component while leaving the  $n>1$  materials behind. In order to investigate various systems a single run of BATQ was prepared as described above. Single gram sample samples of this material were then treated under a variety of precipitation conditions. The results of this work can be seen in Tables 1 and 2.

Trends in these precipitation conditions can be noted. Generally, the lower ratios of precipitant to solvent are more effective at removing BA-DAB-BA. This can be seen in comparisons of samples 4 and 7. Additionally, the higher ml solvent/g BATQ ratios were much more effective than those in which more concentrated solutions were used. Other features of the precipitating solvents also were important. For example, in hexane solutions, apparently some critical point is reached where the product no longer precipitates at all, but instead forms an unfilterable suspension.

The results of this work indicate that the best system involves Sample 7, the use of 10ml tetrahydrofuran per gram BATQ-H sample with precipitation into 15ml methanol. Almost 90% of the starting material was recovered by this method while the BA-DAB-BA content was lowered from 11.9% to 4.5%. In addition, the precipitated material was easy to filter, especially when compared to the chloroform/hexane system (Sample 6) which provided the only comparable reduction in BA-DAB-BA content.

The filtrate from the precipitation of Sample 7 was also reduced to dryness to investigate the exclusiveness of BA-DAB-BA removal. When this dried material was analyzed by liquid chromatography, it was found to be 83.3% BA-DAB-BA and 13%  $n=1$  BATQ-H. This indicates an efficient removal system for  $n=0$  material.

The significant finding is that BA-DAB-BA can be removed with good efficiency from BATQ-H samples. In addition, the room temperature reaction conditions provide the opportunity to obtain purer initial materials.

TABLE 1

## PRECIPITATION CONDITIONS FOR BATQ-H SAMPLES

<u>Sample</u>	<u>Solvent System<sup>a</sup></u>	<u>ml Solvent g BATQ-H<sup>b</sup></u>	<u>% Recovery<sup>c</sup></u>
Initial	-	-	-
1	1:1½ CHCl <sub>3</sub> :MeOH	10	72.5
2	1:1½ THF:MeOH	10	92.0
3	1:1½ THF:MeOH	10	90.5
4	1:3 THF:MeOH	27	94.9
5	1:3 THF:MeOH	14	94.7
6	1:3 CHCl <sub>3</sub> :hexane	27	89.6
7	1:1½ THF:MeOH	20	89.0
8	1:3 CHCl <sub>3</sub> :hexane	10	d
9	1:3 THF:hexane	10	d

a Ratio of the relative volume of solvent to precipitant.

b Volume of solvent used to dissolve 1g BATQ-H.

c Wt % of sample recovered from precipitation.

d Formed an unfilterable suspension.

TABLE 2

## BA-DAB-BA REMOVAL FROM BATQ-H SAMPLES

<u>Sample</u>	<u>% BA-DAB-BA<sup>a</sup></u>	<u>% n=1 BATQ-H<sup>a</sup></u>	<u>% n 1 BATQ-H<sup>a</sup></u>
Initial	11.9	46.0	42.1
1	11.1	46.6	42.3
2	9.6	45.6	44.8
3	8.3	46.8	44.9
4	7.9	48.1	44.0
5	7.6	48.3	44.1
6	4.7	48.8	46.5
7	4.5	48.8	46.7
8	b	-	-
9	b	-	-

a Percents determined by liquid chromatography.

b Formed an unfilterable suspension.

### SECTION III

#### EXPERIMENTAL

3,3'-Diaminobenzidine (DAB) was prepared by a previously described method (Reference 6) and was purified by recrystallization of 50g batches from 3L of water containing 30g of sodium dithionite and 5g of charcoal. The mixture was boiled for 10 minutes, filtered under a nitrogen atmosphere, and allowed to cool under a nitrogen atmosphere. A second recrystallization was carried out using the same conditions and proportions of materials except that no charcoal was used. The crystals were dried in a vacuum oven for 3 hours at 95-100°C to afford recoveries of 60-80%, m.p. 173-175°C, depending upon the purity of the crude DAB.

4-(3-Ethynylphenoxy)benzil was prepared by a previously described method (Reference 1) and recrystallized from methanol, m.p. 82-83°C.

1,4-Bis(4-benzilyloxy)benzene was prepared by a previously described method (Reference 7).

BA-DAB-BA: A mixture of DAB (21.4g) and 4-(3-ethynylphenoxy)benzil (65.2g) was stirred under nitrogen in methanol (1600 mL) until dissolved. Acetic acid (32mL) was added, and the reaction mixture was stirred overnight. A voluminous yellow precipitate formed during this time. The precipitate was filtered, washed in a blender with methanol (2x1600mL), and dried in a vacuum oven at 80° for 3 hours to afford 77.7g (97.8%) of BA-DAB-BA. Eight batches of BA-DAB-BA prepared by the above procedure were combined.

BATQ-H and oligomers: A solution of 1,4-bis(4-benzilyloxy)benzene (0.05 mole) in m-cresol (125 mL) was added dropwise over thirty minutes to a m-cresol (300 mL) solution of 3,3'-diaminobenzidine (0.10 mole) which was stirring at ambient temperature under nitrogen. The reaction was stirred for

four hours following the completion of addition, after which time the end-capping agent, 4-(3-ethynylphenoxy)benzil (0.10 mole), was added to the reaction vessel. The mixture was stirred at ambient temperature for approximately eighteen hours, and it was then precipitated into a 10% solution of sodium hydroxide in methanol (2L). The product was filtered, dried, and then re-precipitated from chloroform (750 mL) into methanol (4 L). Yields averaged 91% at this stage.

BATQ-H Purification: Samples of the BATQ-H were precipitated under a variety of conditions to determine those which removed the greatest amount of  $n=0$  material (BA-DAB-BA). In each case the relative amounts of BA-DAB-BA and monomeric BATQ-H were determined by liquid chromatography. The liquid chromatography was done using four 500 $\text{\AA}$   $\mu$  styragel columns from Waters Associates. Elution was with tetrahydrofuran at a flow rate of 1 ml/min.



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